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⑰ **Method of manufacturing a scandate dispenser cathode and dispenser cathode manufactured by means of the method.**

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Description

The invention relates to a method of manufacturing a scandate dispenser cathode having a matrix at least the top layer of which at the surface consists substantially of tungsten (W) and scandium oxide (Sc₂O₃), and having emissive material in or below said matrix.

The invention also relates to a scandate dispenser cathode manufactured by means of this method.

The invention moreover relates to a method of manufacturing a powder of tungsten grains which are covered at least partly with scandium hydride (ScH₂).

Such cathodes are used as an electron source in display tubes, camera tubes, oscilloscope tubes, klystrons, transmitter tubes, etc.

Such dispenser cathodes have for their property that there is a functional separation between on the one hand the electron emissive surface and on the other hand a store of the emissive material which serves to produce a sufficiently low work function of said emissive surface. One of the types of dispenser cathodes is the L-cathode. The emission of an L-cathode takes place from the surface of a porous matrix of, for example, tungsten, the work function of which is reduced by adsorbed barium (Ba) and oxygen (O). Below said matrix the L-cathode has a storage space in which a mixture of tungsten powder and emissive material, for example, barium-calcium aluminate, is present. The adsorbate at the surface is maintained by means of reactions of the said mixture. A second type of dispenser cathode is the impregnated cathode which is obtained by impregnating a compressed and sintered porous tungsten body with emissive material. In this case the required adsorbate is obtained by means of reaction of the emitter material with the tungsten of the matrix.

A method of the type described in the opening paragraph is known from EP—A—0091161. The advantages of the dispenser cathodes manufactured according to this known method are a good life and a reasonable to moderate recovery after ion bombardment.

It is therefore an object of the invention to provide a method of manufacturing a scandate dispenser cathode having a better recovery after ion bombardment. Another object of the invention is to provide a cathode in which the scandium is distributed more homogeneously in the tungsten matrix than in cathodes comprising scandium oxide grains.

Still a further object of the invention is to provide a method of manufacturing a powder consisting of tungsten grains which are covered at least partly with scandium hydride, which powder is used in the method according to the invention of manufacturing a scandate dispenser cathode.

A method of the kind described in the opening paragraph is characterized according to the invention in that it comprises the following steps:

- a) compressing tungsten powder to form a porous plug;
- b) heating said plug in a non-reactive atmosphere and in contact with scandium to above the melting temperature of scandium;
- c) cooling the plug in a hydrogen (H₂) atmosphere;
- d) pulverizing the plug to form fragments;
- e) heating said fragments to approximately 800°C and firing at this temperature for a few to a few tens of minutes in a hydrogen atmosphere and cooling in said hydrogen atmosphere;
- f) grinding the fragments to scandium hydride—tungsten powder (ScH₂/W);
- g) compressing a matrix or a top layer on a matrix of pure tungsten from said ScH₂/W powder or from a mixture of said powder with tungsten powder;
- h) sintering and cooling said matrix;
- i) bringing emissive material in the cathode.

Experiments have demonstrated that a coating of the order of magnitude of a mono-layer of barium on bulk scandium oxide does not give rise to a high emission. Furthermore, the reaction of scandium oxide with tungsten and tungsten oxide is of importance for the oxygen system on the surface of the cathode. It is hence of importance to have scandium oxide in contact with tungsten. The use of scandium oxide grains does not seem to be best solution for this purpose, because in fact the core of the grain will not contribute to the desired processes. By using the method according to the invention, the tungsten grains in the cathode surface are partly covered with scandium oxide or scandium having scandium oxide thereon. Of course, a more homogeneous distribution of scandium over the cathode surface is obtained than is the case when a mixture of scandium oxide grains and tungsten grains is used.

The porous plug of tungsten powder (step a) is compressed, for example, to a density of approximately 60% of the density of tungsten metal.

The plug is heated (step b) in a non-reactive atmosphere, but preferably in a vacuum, because then a good coating of the tungsten with scandium is obtained. The tungsten is coated by heating the plug in contact with scandium to above the melting temperature of scandium, as a result of which the melted scandium is drawn into the pores of the porous plug. The scandium may be provided on the plug, for example, in the form of a lump of scandium. For example, approximately 3% by weight of scandium is taken up in the plug. The plug is then cooled in hydrogen (step c) as a result of which it becomes brittle due to the fact that the scandium is partly converted into scandium hydride, an increase in volume occurring. As a result of this, the plug may then be pulverized (step d). The fragments are then heated in a molybdenum crucible in a hydrogen atmosphere up to 800°C and kept at this temperature for approximately 15 minutes

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and slowly cooled in said same hydrogen atmosphere, substantially all the scandium being converted into scandium hydride (step e). The fragments are then ground in an agate mill to grains of the desired size (step f). Scandium hydride is a stable compound. The resulting powder may hence be stored in air.

Upon sintering a cathode matrix, the scandium hydride is decomposed (above 800°C). Because scandium hydride has a larger specific volume than scandium, it is therefore to be preferred upon sintering and cooling in hydrogen, to remove the hydrogen at a temperature above 800°C by pumping. Upon sintering in a vacuum, this problem does not occur. However, in that case special measures must be taken to avoid excessive scandium evaporation. It is possible indeed upon sintering and cooling in hydrogen to obtain a good result when the powder manufactured in step f) is provided as a top layer on the tungsten matrix, in particular when said powder is dehydrogenated or is mixed with 25 to 75% by weight of tungsten powder, preferably approximately 50% by weight of tungsten powder. Such a top layer preferably has a thickness which is smaller than 0.15 mm. As an impregnant in the cathodes to be described hereinafter, a conventional barium-calcium aluminate has been used. The whole or partial oxidation of the scandium present on the tungsten grains takes place during the manufacture of the cathode, for example, upon impregnating and/or activating. It is to be noted in this connection that scandium oxide thermodynamically is more stable than barium oxide.

The invention will now be described in greater detail, by way of example, with reference to a number of specific examples and a drawing, in which

Figure 1 is a side sectional view of an impregnated cathode according to the invention, and Figure 2 is a side sectional view of an L-cathode according to the invention.

Figure 1 is a side sectional view of a scandate dispenser cathode according to the invention. A cathode body 1 having a diameter of 1.8 mm has been obtained by compressing a matrix having a top layer 2 from the powder according to step f) of claim 1. This powder consists of tungsten grains which are covered at least partly with scandium hydride. After sintering and cooling, the cathode body 1 consists of an approximately 0.1 mm thick scandium oxide and a scandium-containing porous tungsten layer on a porous tungsten layer having a thickness of approximately 0.4 mm. The cathode body is then impregnated with barium-calcium aluminate. Said impregnated cathode body, whether or not compressed in a holder 3, is welded on the cathode shank 4. A helical cathode filament 5 which may consist of a helically wound metal core 6 with an aluminium oxide insulation layer 7 is present in the cathode shank 4.

The recovery after ion bombardment in a cathode is important for use in various types of electron tubes. During the processing and/or during operation, cathodes in tubes are exposed to a bombardment of ions originating from residual gases. This recovery was measured on diodes having an anode which can be fired separately from the cathode in a high-vacuum arrangement. The emission is measured in a 1500 V pulse across the diode with an electrode spacing cathode-anode distance of 300 µm. After activating the cathode in a vacuum, 10^{-5} torr argon were introduced into the system. With 1.5 kV pulses at the anode (10 Hz frequency) with such a pulse length that at the beginning the anode dissipation is 5 Watts, current was drawn for 40 minutes, said current gradually decreasing more or less. The cathode temperature (molybdenum brightness) was 1200 K. The argon was then removed by pumping. Recovery of the cathode then occurred at 1200 K with a current of density of 1 A/cm² for 2 hours, succeeded by 1 hour at 1320 K at 1 A/cm². During this recovery the current during a 1500 V pulse on the anode was measured every 10 minutes and compared with the starting value. The said cycle of sputtering and recovery was then repeated once again. The current measured immediately after activation in a 1500 V pulse is indicated by $I(O)_{1500}$ and the value measured after the described two cycles by $I(e)_{1500}$. The ratio $I(e)_{1500}/I(O)_{1500}$ is a measure of the recovery H (%) after ion bombardment. Prior art cathodes and cathodes according to the invention sintered at various temperatures T_s (°C) are compared with each other in the table below. In order to obtain a fair mutual comparison, it has been ensured that the porosity, i.e. the absorbed quantity of impregnant (Imp." expressed in the table in % by weight) was always the same, as well as possible, by varying the pressure with the sintering temperature in an adequate manner.

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TABLE

		P (atm)	T_s (°C)	Imp wt. %	I_{1000} (mA)	H (%)
55	Sc ₂ O ₃ +W top layer on W	2	1900	4.2	3000	65
	50% ScH ₂ /W +50% W	4	1500	4.2	3000	80
60	top layer on W	2.5	1800	4.2	2600	55

The matrixes having a top layer of 50% ScH₂/W (i.e. W partly covered with ScH₂) mixed with 50% W showed a much more homogeneous scandium distribution than the known matrixes having an Sc₂O₃+W (i.e. mixture of Sc₂O₃ grains and W grains) top layer. In addition, the recovery of a cathode manufactured

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with ScH_2/W and sintered at 1500°C after ion bombardment is significantly better than for the known $\text{Sc}_2\text{O}_3+\text{W}$ top layer cathode ($H=80\%$ as against $H=65\%$). It also follows from this table how the sintering temperature for ScH_2/W cathodes influences the emission as measured in a 1000 V pulse and the recovery after ion bombardment. Sintering is preferably carried out at a temperature lower than the melting-point of scandium, namely 1541°C . The emission during a 1000 V pulse, also for ScH_2/W cathodes having a top layer on the W matrix of 25% of the ScH_2/W powder with 75% W powder and sintered at 1500°C , is again 3000 mA with approximately the same impregnant consumption. This is the case also for an ScH_2/W top layer to which no W has been added and for a top layer consisting of a 1:1 mixture of ScH_2/W powder and W powder on a W matrix in which the material was compressed more heavily (impregnant consumption 3%).

Figure 2 is a side sectional view of an L-cathode according to the invention. The cathode body 10 has been compressed from a mixture of 25% ScH_2/W and 75% W and has then been sintered. This cathode body 10 has been placed on a molybdenum cathode shank 11 having an upright edge 12. A cathode filament 13 is present in the cathode shank 11. A store 15 of emissive material (for example, barium-calcium aluminate mixed with tungsten) is present in the hollow space 14 between the cathode body 10 and the cathode shank 11.

Claims

1. A method of manufacturing a scandate dispenser cathode having a matrix at least the top layer of which at the surface consists substantially of tungsten (W) and scandium oxide (Sc_2O_3) and having emissive material in or below said matrix, characterized in that it comprises the following steps:
 - a) compressing tungsten powder to form a porous plug;
 - b) heating said plug in a non-reactive atmosphere and in contact with scandium to above the melting temperature of scandium;
 - c) cooling the plug in a hydrogen (H_2) atmosphere;
 - d) pulverizing the plug to fragments;
 - e) heating the fragments to approximately 800°C and firing them at this temperature in a hydrogen atmosphere for a few to a few tens of seconds and cooling in said hydrogen atmosphere;
 - f) grinding the fragments to scandium hydride-tungsten powder (ScH_2/W);
 - g) compressing a matrix or a top layer on a matrix of pure tungsten from this ScH_2/W powder or from a mixture of this powder with tungsten powder;
 - h) sintering and cooling the said matrix;
 - i) bringing emissive material in the cathode.
2. A method as claimed in Claim 1, characterized in that in step b) the plug is heated in a vacuum.
3. A method as claimed in Claim 1 or 2, characterized in that in step b) the scandium is provided on the plug.
4. A method as claimed in Claim 1, 2 or 3, characterized in that step h) is carried out in a hydrogen atmosphere and the hydrogen is removed by pumping at a temperature above 800°C .
5. A method as claimed in Claim 1 or 2, characterized in that in step g) the ScH_2/W is provided in the form of a top layer on a tungsten matrix and that step h) is carried out in hydrogen.
6. A method as claimed in Claim 5, characterized in that the ScH_2/W in the top layer is mixed with W, the mixing ratio being approximately 1:1.
7. A method as claimed in Claim 5 or 6, characterized in that the thickness of the top layer is smaller than approximately 0.15 mm.
8. A method as claimed in Claim 1, 2 or 3, characterized in that step h) is carried out in a vacuum.
9. A method as claimed in any of the preceding claims, characterized in that sintering is carried out at a temperature lower than the melting-point of scandium, being 1541°C .
10. A method of manufacturing a powder consisting of tungsten grains which are covered at least partly with scandium hydride, characterized in that the said method comprises the steps a) to f) as claimed in Claim 1.
11. A method as claimed in Claim 10, characterized in that in step b) the plug is heated in a vacuum.
12. A method as claimed in Claim 10 or 11, characterized in that in step b) the scandium is provided on the plug.
13. A scandate dispenser cathode manufactured by a method as claimed in any of the Claims 1 to 9, characterized in that said cathode at the surface comprises tungsten grains, which are partly covered with scandium oxide or scandium having thereon scandium oxide.
14. A scandate dispenser cathode manufactured by a method as claimed in any of the Claims 1 to 9, or as defined in Claim 13, characterized in that the absorbed quantity of impregnant is 2 to 6% by weight of the matrix.
15. An electron tube comprising a scandate dispenser cathode as claimed in Claim 13 or 14.

Patentansprüche

1. Verfahren zur Herstellung einer Scandat-Vorratskathode mit einer Matrix, von der wenigstens die

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Deckschicht an der Oberfläche im wesentlichen aus Wolfram (W) und Scandiumoxid (Sc_2O_3) besteht und mit in oder unter dieser Matrix vorhandenem Emitttermaterial, dadurch gekennzeichnet, dass das Verfahren die folgenden Verfahrensschritte aufweist:

- a) das Pressen eines porösen Pfropfens aus Wolframpulver;
 - 5 b) das Erhitzen dieses Pfropfens in einer nicht reaktiven Atmosphäre und in Kontakt mit Scandium bis über die Schmelztemperatur von Scandium;
 - c) das Abkühlen des Pfropfens in einer Wasserstoffatmosphäre (H_2);
 - d) das Zerpulvern des Pfropfens zu Bruchteilen;
 - e) das Erhitzen der Bruchteile bis etwa 800°C und das Brennen derselben bei dieser Temperatur in einer
 - 10 Wasserstoffatmosphäre während einiger bis zu einigen zehn Sekunden sowie das Abkühlen derselben in der genannten Atmosphäre;
 - f) das Zermahlen der Bruchteile zu Scandiumhydridwolframpulver (ScH_2/W);
 - g) das Pressen einer Matrix oder einer Deckschicht auf einer Matrix aus reinem Wolfram aus diesem ScH_2/W -Pulver oder aus einem Gemisch dieses Pulvers mit Wolframpulver;
 - 15 h) das Sintern und Abkühlen dieser Matrix;
 - i) das in die Kathode Einbringen des Emitttermaterials.
2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, dass in dem Verfahrensschritt b) der Pfropfen im Vakuum erhitzt wird.
 3. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, dass in dem Verfahrensschritt b) das
 - 20 Scandium auf dem Pfropfen angebracht wird.
 4. Verfahren nach Anspruch 1, 2 oder 3, dadurch gekennzeichnet, dass der Verfahrensschritt h) in einer Wasserstoffatmosphäre durchgeführt und der Wasserstoff bei einer Temperatur über 800°C abgepumpt wird.
 5. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, dass in dem Verfahrensschritt g) das
 - 25 ScH_2/W in Form einer Deckschicht auf einer Wolframmatrix angebracht wird und dass der Verfahrensschritt h) in Wasserstoff durchgeführt wird.
 6. Verfahren nach Anspruch 5, dadurch gekennzeichnet, dass das ScH_2/W in der Deckschicht mit W vermischt wird, wobei das Mischverhältnis etwa 1:1 beträgt.
 7. Verfahren nach Anspruch 5 oder 6, dadurch gekennzeichnet, dass die Dicke der Deckschicht weniger
 - 30 als etwa 0,15 mm beträgt.
 8. Verfahren nach Anspruch 1, 2 oder 3, dadurch gekennzeichnet, dass der Verfahrensschritt h) im Vakuum durchgeführt wird.
 9. Verfahren nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, dass das Sintern bei einer Temperatur unter dem Schmelzpunkt von Scandium, d.h. 1541°C ; erfolgt.
 - 35 10. Verfahren zur Herstellung eines Pulvers aus Wolframkörnern, die wenigstens teilweise mit Scandiumhydrid bedeckt sind, dadurch gekennzeichnet, dass dieses Verfahren die Verfahrensschritte a) bis f) nach Anspruch 1 umfasst.
 11. Verfahren nach Anspruch 10, dadurch gekennzeichnet, dass in dem Verfahrensschritt b) der Pfropfen im Vakuum erhitzt wird.
 - 40 12. Verfahren nach Anspruch 10 oder 11, dadurch gekennzeichnet, dass in dem Verfahrensschritt b) das Scandium auf dem Pfropfen angebracht wird.
 13. Skandat-Vorratskathode, hergestellt nach einem Verfahren nach einem der Ansprüche 1 bis 9, dadurch gekennzeichnet, dass diese Kathode an der Oberfläche Wolframkörner aufweist, die teilweise mit Scandiumoxid oder mit Scandium, auf dem sich Scandiumoxid befindet, bedeckt sind.
 - 45 14. Skandat-Vorratskathode, hergestellt nach einem Verfahren nach einem der Ansprüche 1 bis 9 oder wie im Anspruch 13 definiert, dadurch gekennzeichnet, dass die absorbierte Menge Imprägnierungsmittel 2 bis 6 Gew.% der Matrix beträgt.
 15. Elektronenröhre mit einer Skandat-Vorratskathode nach Anspruch 13 oder 14.

50 Revendications

1. Procédé pour la fabrication d'une cathode à réserve à base de scandate, comprenant une matrice dont au moins la surface de la couche supérieure est constituée essentiellement par du tungstène (W) et de
- 55 l'oxyde de scandium (Sc_2O_3) et dans laquelle ou au-dessous de laquelle se trouve du matériau émissif, caractérisé en ce qu'il comprend les étapes suivantes:
 - a) pressage de poudre de tungstène pour former un bouchon poreux;
 - b) chauffage dudit bouchon dans une atmosphère non réactif et en contact avec du scandium jusqu'au-dessus de la température de fusion du scandium;
 - 60 c) refroidissement du bouchon dans une atmosphère d'hydrogène (H_2);
 - d) pulvérisation du bouchon pour former des fragments;
 - e) chauffage desdits fragments jusqu'à environ 800°C et chauffage à cette température pendant quelques minutes à quelques dizaines de minutes dans une atmosphère d'hydrogène et refroidissement dans ladite atmosphère d'hydrogène;
 - 65 f) meulage des fragments en poudre de tungstène-hydruure de scandium (ScH_2/W);

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- g) pressage d'une matrice ou d'une couche supérieure sur une matrice en tungstène pur à partir de ladite poudre de ScH_2/W ou à partir d'un mélange de ladite poudre avec de la poudre de tungstène;
 h) frittage et refroidissement de ladite matrice;
 i) introduction d'un matériau émissif dans la cathode.
- 5 2. Procédé selon la revendication 1, caractérisé en ce que dans l'étape b) le bouchon est chauffé sous vide.
3. Procédé selon la revendication 1 ou 2, caractérisé en ce que dans l'étape b), le scandium est appliqué sur le bouchon.
4. Procédé selon la revendication 1, 2 ou 3, caractérisé en ce que l'étape h) est effectuée dans une
 10 atmosphère d'hydrogène et l'hydrogène est enlevé par pompage à une température supérieure à 800°C .
5. Procédé selon la revendication 1 ou 2, caractérisé en ce que dans l'étape g), le ScH_2/W est appliqué sous forme d'une couche supérieure sur une matrice en tungstène et que l'étape h) est effectuée dans de l'hydrogène.
6. Procédé selon la revendication 5, caractérisé en ce que le ScH_2/W dans la couche supérieure est
 15 mélangé avec W, le rapport de mélange étant d'environ 1:1.
7. Procédé selon la revendication 5 ou 6, caractérisé en ce que l'épaisseur de la couche supérieure est inférieure à environ 0,15 mm.
8. Procédé selon la revendication 1, 2 ou 3, caractérisé en ce que l'étape h) s'effectue sous vide.
9. Procédé selon l'une des revendications précédentes, caractérisé en ce que le frittage s'effectue à une
 20 température inférieure au point de fusion du scandium, c'est-à-dire 1541°C .
10. Procédé pour la préparation d'une poudre constituée par des grains de tungstène qui sont recouverts au moins partiellement d'hydruure de scandium, caractérisé en ce que ledit procédé comprend les étapes a) à f) selon la revendication 1.
11. Procédé selon la revendication 10, caractérisé en ce que dans l'étape b), le bouchon est chauffé
 25 sous vide.
12. Procédé selon la revendication 10 ou 11, caractérisé en ce que dans l'étape b), le scandium est appliqué sur le bouchon.
13. Cathode à réserve à base de scandate réalisée par un procédé selon l'une des revendications 1 à 9, caractérisée en ce qu'à la surface ladite cathode comporte des grains de tungstène qui sont partiellement
 30 recouverts d'oxyde de scandium ou de scandium présentant de l'oxyde de scandium.
14. Cathode à réserve à base de scandate réalisée par un procédé selon l'une des revendications 1 à 9 ou comme défini dans la revendication 13, caractérisée en ce que la quantité absorbée de substance d'impregnation est de 2 à 6% en poids de la matrice.
15. Tube électronique comportant une cathode à réserve à base de scandate selon la revendication 13
 35 ou 14.

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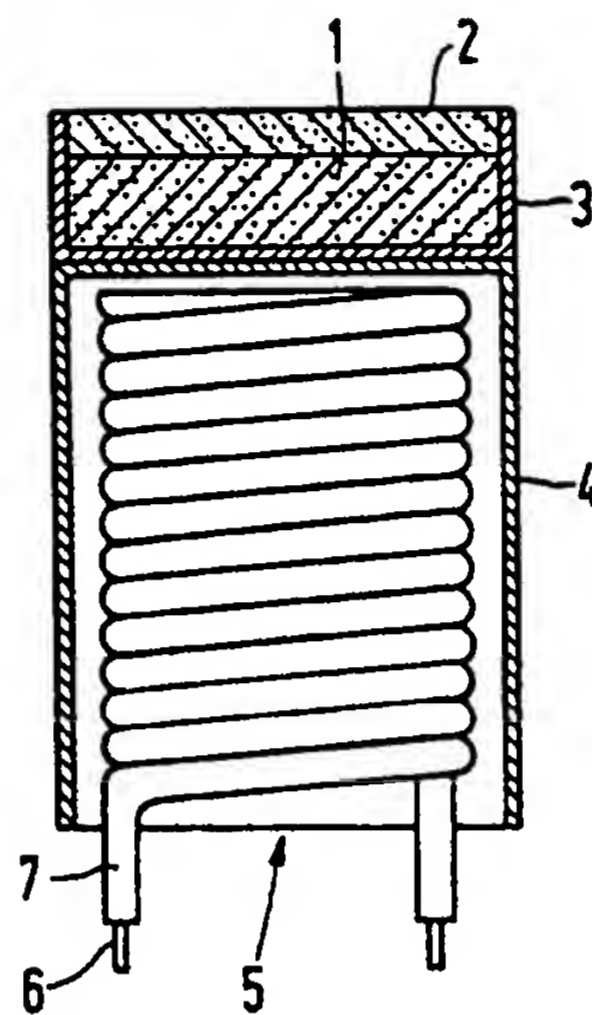


FIG.1

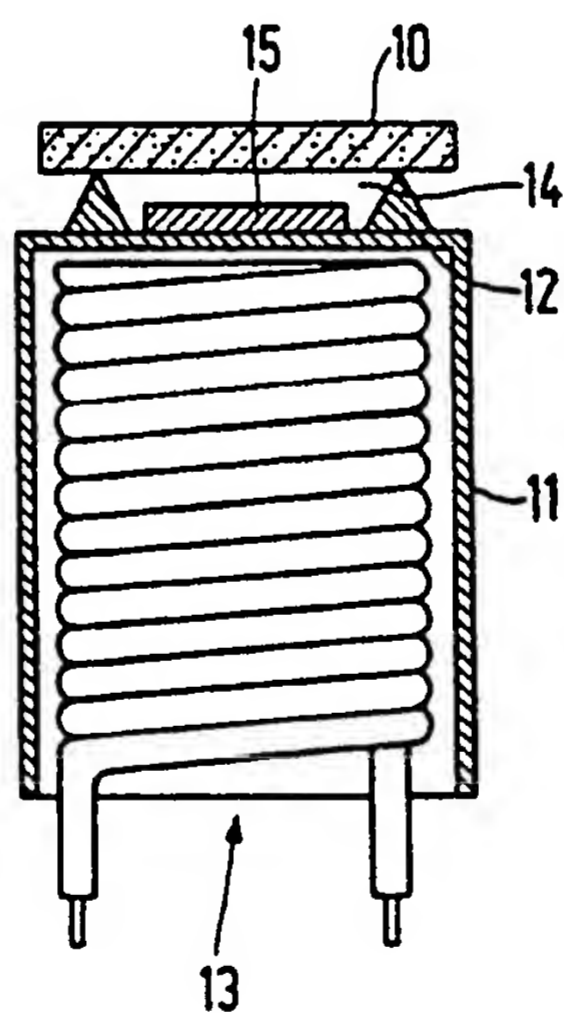


FIG.2